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The Chlorides
of
Paranitroorthosulphobenzoic acid.

Dissertation

Submitted to the Board of University Studies of the Johns Hopkins University for the Degree of Doctor of Philosophy.

By

G. Wm Gray.

1895

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This work was suggested by Professor Remsen and was carried out under his direct supervision. To him I desire to express my sincere thanks for the instruction received in the laboratory as well as in the lecture room. I also wish to express my obligation to Professors A. A. Morse and W. B. Clark of the Geological Dept.

The Chlorides of Paramido orthosulphotungstic acid.

1 Introduction.

In the course of an investigation on the action of aniline upon the chloride of orthosulphotungstic acid Remsen and Coates¹ in 1891 obtained two isomeric anilides, with quite different properties, and an anal. This suggested that the chloride was not an individual. In the following year Remsen and Kohler² obtained fairly conclusive evidence of the existence of two chlorides, one of which they obtained as a pure crystalline product, the other as an oil. The crystalline chloride on treatment with aniline

¹ Amer. Chem. Jour. 14, 2311

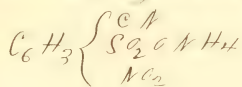
² " " " " 330

yielded only the products she first
described and she and the others
yielded besides these two products an
unfused oxide. Remsen and Sunder-
s' the next year, obtained both
chlorides in crystalline form.

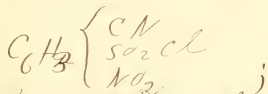
In consequence of this work
it was deemed ^{advisable} to study the
action of phosphorus pentoxide
upon paranthrobesulphonic
acid and see if it would
yield isomeric chlorides. The re-
sults which I have obtained and
which are given in detail on the
following pages show that two
chlorides are obtained, though
Muller² describes only one as the
product of such action.

In this article I shall speak of

the two chlorides as the symmetrical and the unsymmetrical. The evidence which leads to this view is obtained from the action of ammonia upon the two chlorides. When the unsymmetrical chloride is treated with ammonia, it is converted into the ammonium salt of para-nitrocyano benzenesulphonic acid

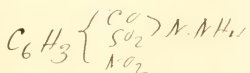


and this compound can be converted into a chloride by treatment with phosphorus pentachloride



on the other hand the symmetrical chloride gives with

ammonia, the ammonium salt
of paratoluenic sulphimide.
This ammonium salt



on treatment with acids, gives
paratoluenic sulphimide, which
crystallizes in fine needles and
melts at 209°

Preparation of Material

100 grams of paratoluenic amine
mixed with 400 grams of fuming
sulphuric acid and heated
in a balloon flask at a tem-
perature of 100° , by being immers-
ed in boiling water. The mixture
was kept at this temperature for

til a portion of it can be g
forced into water, goes slowly
ly into solution. This heating
usually requires from 1 to 8 hours.
The mixture is then allowed to
cool and poured into cold
water. After standing for several
hours, it is filtered and then
neutralized with calcium carbon-
ate. The calcium salt is filtered
from the calcium sulphate and
converted into the potassium
salt by treatment with potas-
sium carbonate. The potassium
salt is filtered from the calcium
carbonate and evaporated to crys-
tallization. 100 grams of the
potassium salt of peroxynitrous
sulphonic acid. Together with 30

grams of potassium hydroxide are dissolved in 5000 cc of water; the balloon-flask containing this solution is immersed in water and heated to a temperature of 100° . When the solution has acquired this temperature 220 grams of potassium permanganate are added, and the mixture heated until the color of the permanganate has entirely disappeared. The amber-colored liquid is then filtered from the manganese hydrate, and the dark brown residue thoroughly washed with hot water. The filtrate and washings are then neutralized with hydrochloric acid, and evaporated until the neutral potassium salt begins



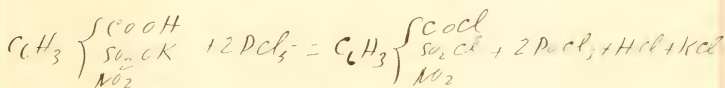
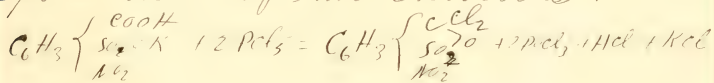
to crystallize out, when a small quantity of the solution is cooled. The whole solution is then allowed to cool and strong hydrochloric acid added in excess, when the acid potassium salt of paranitroorthosulphobenzoic acid separates out in beautiful fine white needles.

III Action of Phosphorus Pentachloride upon the Acid Potassium Salt of Paranitroorthosulphobenzoic Acid

When one molecule of the anhydrous acid potassium salt of paranitroorthosulphobenzoic acid is intimately mixed with two molecules of phosphorus pentachloride

no action - or only very slight action takes place in the cold. 140 grams of the acid potassium salt are mixed with 60 grams of phosphorus pentachloride and heated in a distilling-bulb at a temperature of 150° . The distilling-bulb is immersed in a sulphuric acid bath and kept at a temperature of 150° for four or five hours.

Reaction takes place with the formation of two chlorides:



The yield of the first is from 80-90% and of the second from 10-20%. The chlorides must not be heated

much above 130° as decomposition begins at 1700° . The yield of the second chloride is increased to about 30% by heating in an open dish upon the water-bath. The oily mass is poured into water and washed free from phosphorus trichloride and potassium chloride. The chlorides are then dissolved in chloroform, the chloroform solution dried by means of calcium chloride; after filtering off the calcium chloride, the solution is allowed to evaporate slowly in a bell-jar free from moist air. From this solution a considerable quantity of the solid chloride (symmetrical) is obtained in crystals which look as if they consisted of monoclinic(?)

prisms and basal planes. These crystals are filtered off and washed with ice-cold chloroform. After no more crystals can be obtained by this method, more chloroform is added and the solution transferred to an Erlenmeyer flask. This flask is immersed in a freezing-mixture of salt and ice and dry air drawn over the solution for several days. From this solution more crystals of the symmetrical chloride are obtained, these are filtered off and washed very quickly with cold chloroform. The chloroform solution was repeated until all the chloroform had been driven off, and the oil was then dissolved in a large volume of petroleum ether.

16
(boiling-point 55° - 90°). As the ether solution cools, it becomes cloudy and then begins to clear up. When this happens pour the solution into another beaker and allow the solution to continue to cool. From this solution the unsymmetrical chloride then crystallizes almost pure.

This (unsymmetrical) chloride is slightly soluble in petroleum ether 1 pt in 200, and crystallizes from this solvent in fine needles or long flat plates up to 3 to 4 mm broad and 2 to 3 cm long. They are extremely soluble in ether and chloroform, but crystals can not be obtained from these solvents. It is decomposed on heating above 160° .

and melts at $56-57^{\circ}$ (Uncor) This chloride is probably identical with that obtained by Kastle¹

The symmetrical chloride can be obtained pure by recrystallizing the first crystals obtained above. It can also be obtained by dissolving the two chlorides in chloroform and shaking this solution with a little dilute ammonia. The ammonia will act immediately upon the unsymmetrical chloride, and very slightly upon the symmetrical. The chloroform solution is washed free from ammonia, and dried by means of calcium chloride and allowed to evaporate. From the chloroform solution beautiful crystals are obtained which ap-

78
appear to consist of a combination
of monoclinic pinacoids and
basal planes. It is also soluble
in ether but less so than the iso-
meric chloride. It melts at 94° - 95° (uncor-
rected). It can be heated in a sealed tube
with phosphorus oxychloride to
a temperature of 150° without under-
going any decomposition.

Both chlorides when in crystalline
form, can be left exposed air
to moist air without undergoing
very much decomposition. When
the chlorides are first formed -
if crystals are obtained - decom-
position goes on more readily
judging from the amount of
hydrochloric acid given off.

Analyses of the Chlorides

Portions of both chlorides were heated in a sealed tube with fuming nitric acid. The results obtained were as follows:

0.1933 gr unsym. chloride	gave	0.1763 ^{gr} AgCl
0.1933 "	"	" 0.1585 BaSO ₄
0.1927 "	"	" 0.1950 AgCl
0.1927 "	"	" 0.1548 BaSO ₄

Calculated for	Found	
$C_6H_3 \begin{cases} 5 CCl_2 \\ 3 O_2 \\ 11 H_2 \end{cases}$	I	II
Cl - 24.97	25.00	25.02
S 11.25	11.28	11.06

The symmetrical chloride on analysis gave
 0.1901 ^{gram} sym. chloride gave 0.1935^{gram} AgCl
 0.1830 " " " 0.1875^{gram} AgCl.

Calculated for	Found	
$C_6H_3 \begin{cases} 5 COCl \\ 3 O_2 \\ 11 H_2 \end{cases}$	I	II
Cl 24.97	25.15	25.06

IV Action of Water on the Chlorides

Both water acts very slowly upon the two chlorides, even after several months the decomposition is incomplete. On hot water they are not readily decomposed, but on boiling the decomposition is complete in a few minutes. The decomposition is about as rapid in one case as in another. With dilute caustic potash they are readily decomposed and, after adding an excess of hydrochloric acid was added when the characteristic acid potassium salt of paramecithiosulphobenzoic acid crystallized out in fine needles showing that both yield the same decomposition product.

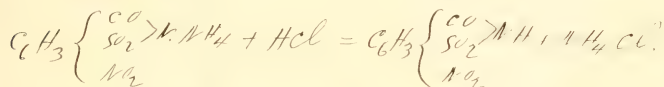
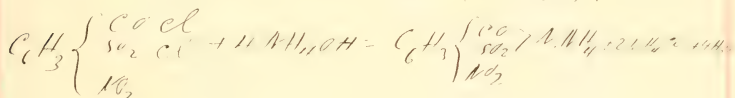


Action of Ammonia upon the Chloride

Kastle mentions a product of the action of ammonia upon the chloride which he obtained but gives no description of it. It was therefore thought best to repeat this work.

5 grams of the symmetrical chloride were dissolved in ether and poured off into a beaker containing 150 cc of dilute ammonia. The solution was allowed to stand for several days until the ether evaporated. From this solution the ammonium salt of succinylglyoxal succinimide was obtained. The yield was theoretical. The crystals are rectangular plates or glistening plates.

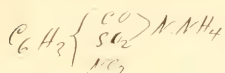
boiling point of sulphurous acid.
 It is also soluble in alcohol. On
 adding metaphosphoric acid to the
 salt, parametabenzic sulphimide
 is obtained. This sulphimide crys-
 tallizes in plates or fine needles
 and melts at 209° (Uncor).



When the perfectly dry chloride
 is dissolved in anhydrous ether
 and dry ammonia gas passed
 into the solution the same prod-
 uct is obtained.

0.3000 grams of the salt gave 0.5116 g. H₂O.
 0.3000 " " " " " 0.5178 " "

calculated for



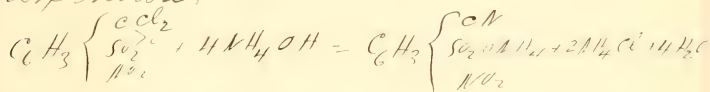
found

T	II
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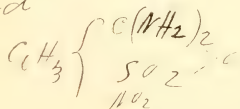
N	17.18	17.16	17.26
---	-------	-------	-------

5 grams of the unsymmetrical chloride were dissolved in ether and poured into a beaker containing 100 cc of dilute ammonia. After the ether had evaporated nothing crystallized from the solution until it had evaporated to about 50 cc when a large mass of needles were obtained. These needles grouped themselves in radiating masses, or tufts. This product proved to be the ammonium salt of para-nitrocybenzene sulphonic acid. This salt is also obtained when the mixed chlorides are dis-

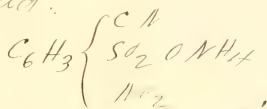
solved in chloroform and shaken with dilute ammonia. From the ammoniacal solution the ammonium salt is obtained on evaporation. From the chloroform solution the symmetrical chloride is obtained. When ammonia is poured upon the unsymmetrical chloride solution take place immediately. In the case of the symmetrical chloride reaction is not complete even after 24 hours.



It is probable that an unstable diamid



is first formed and that this
by an intramolecular change
passes over into the ammonium
salt of paranthocyanbenzene sul-
phonic acid.

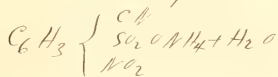


The analysis of this salt gave
the following results:

on standing over sulphuric acid

0.9965 grams lost .0687 grams H_2O

calculated for



Found

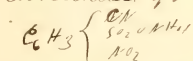
H_2O - 6.85

6.90

0.3000 gram of the anhydrous salt gave 0.65448 g N

0.3000 " " " " " " 0.05796 " "

calculated for



Found

1

11

N 17.18

17.16

17.32

All nitrogen determinations which are given in grams were made by the Kjeldahl method; all others were by the absolute method.

On adding acid to this salt nothing separates out even on boiling. As further study was desired in order to place the formation of this salt beyond doubt, a number of salts derived from these two ammonium salts were made.

VI Ammonia Salts.

a. Silver salts.

Ammon. Para-nitrocyanbenzenesulphate



This salt was prepared by treating ammonium

para-nitrocyanbenzenesulphonate
 with silver nitrate. To the solu-
 tion of the ammonium salt
 silver nitrate is added, and the
 solution allowed to cool. On cool-
 ing the silver salt crystallizes in
 fine long rectangular needles 2 cm
 long. This salt contains one mol-
 ecule of water of crystallization.

0.6744 gram of this salt lost .0354 gram of
 H_2O at 100°

Calculated for



H_2O 5.25 5.10

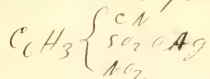
The analysis of the silver salt in analysis
 gave the following results.

0.1779 grams gave .0760 gram $AgCl$

0.1556 " " " 0.667 " "

0.2010 " " " 15.1 cc N

Calculated for



Found

I II

Ag	32.21	32.16	32.26
N	8.38	8.63	

Silver salt of the Sulphinic $C_6H_3 \left\{ \begin{array}{l} CO \\ SO_2 \\ NO_2 \end{array} \right\} Ag$

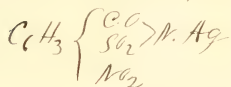
This salt was prepared by adding silver nitrate to the ammonium salt of the sulphinic.

It crystallizes in short fine needles, difficultly soluble in boiling water, insoluble in cold water. It contains no water of crystallization; It turns brown on exposure to the light.

0.1508 gram gave .0645 gram AgCl

0.1993 " " .0856 " "

Calculated for



Found

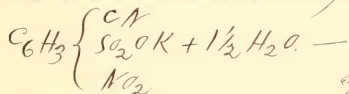
I

II

Ag	32.21	32.20	32.30
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1. The Potassium Salt

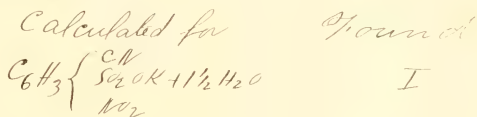
Potassium Para nitro cyanobenzenesulphonat



This salt is prepared by heating the silver salt with sufficient potassium chloride to precipitate all the silver. The solution is filtered from the silver chloride and evaporated to crystallization. The potassium salt crystallizes in beautiful crystals. The crystals are 2 to 3 cm. in length and contains $1\frac{1}{2}$ molecules of water of crystalli-

gulin.

0.3177 gram of this salt lost .0287 gram H_2O at 100°

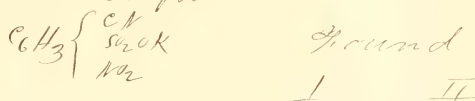


H_2O	9.21	9.03
--------	------	------

0.1868 gram of the anhydrous salt gave .0605 gram K_2SO_4

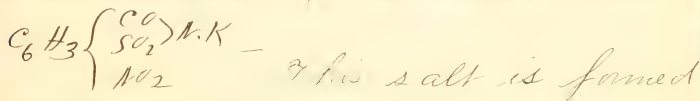
0.2495 gram of the anhydrous salt gave 0.802 gr K_2SO_4

calculated for



K	14.66	14.54	14.43
---	-------	-------	-------

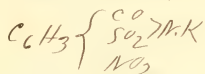
Potassium salt of the trinitrobenzoate



by heating paranthrobenzoic sulphide with potassium carbonate until neutral reaction. It crystallizes in fine leaflets and contains one molecule of crystallization. It is easily ^{soluble} in hot water but difficultly soluble in cold.

0.2352 gram of this salt gave .0757 gram K_2SO_4

calculated for



found

K	14.66	14.45
---	-------	-------

c. The Barium Salt.

Barium Paranthrocyano benzene sulphate

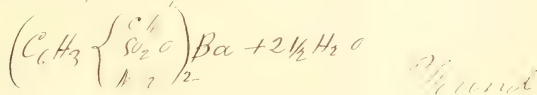
$(C_6H_3 \left\{ \begin{array}{l} CO \\ SO_2O \\ NO_2 \end{array} \right\} Ba + 2\frac{1}{2} H_2O -$ This salt is made by treating the silver salt with bar-

iron chloride. It could not be obtained in well-formed crystals, but formed wet like masses. It is readily soluble in cold water and contains $2\frac{1}{2}$ molecules of water of crystallization

0.3747 gram of this salt lost 0.265 gram H_2O at 100°

0.3698 " " " " " gave 0.1325 gram $BaSO_4$

calculated for



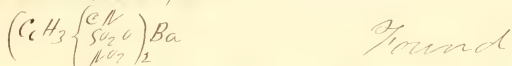
H_2O 7.07 7.07

Ba 21.08 21.23

It loses $\frac{1}{2}$ molecules of water of crystallization on sulfuric acid.

0.2093 gram anhydrous salt gave 0.0822 gram $BaSO_4$

calculated for



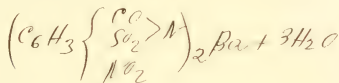
Ba 23.17 23.09

Barium Salt of the Sulphinic Acid $(C_6H_3\{SO_2\}N)_2Ba \cdot 3H_2O$

This salt is obtained by heating the sulphinic acid with barium carbonate. The solution is filtered from the excess of barium carbonate and allowed to crystallize. The salt forms well developed prisms which contain 3 molecules of water of crystallization.

0.3881 gram of this salt = 0.1329 gram H_2O when

calculated for



Found

H_2O

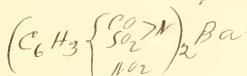
8.37

8.44

0.3552 gram of the anhydrous salt gave 0.1396 gram

$BaSO_4$.

calculated for



Found

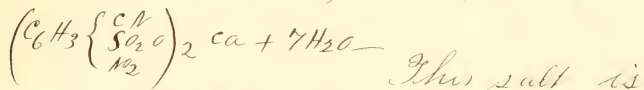
Ba

23.17

23.10

d. The Calcium Salts.

Calcium Para nitro cyanbenzenesulphonate



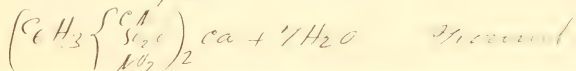
This salt is formed by heating the silver salt with calcium chloride. It, like all the salts of the cyanbenzenesulphonic acid, is extremely soluble in water.

It is, in fact, soluble in less than its own weight of water. It forms flat plates which are elongated. It loses 3 molecules of water on crystallization or sulphuric acid and four more at a temperature of 135°

0.6459 gram of this salt lost 0.0541 gram H_2O or H_2SO_4 sulphuric acid

0.6459 gram of this salt lost 0.1284 gram H_2O at 135°

calculated for



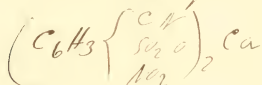
7H₂O

20.31

20.04

0.2429 gram of the anhydrous salt gave
0.0661 gram CaSO₄.

Calculated for



Found

Ca

8.09

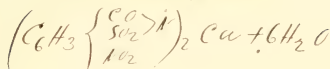
8.10

Calcium Salt of the Sulfonate $\left(C_6H_3 \left\{ \begin{array}{c} SO_2O \\ CH_2 \end{array} \right\} \right)_2 Ca \cdot 6H_2O$

This salt is formed by heating benzoic benzenesulfonate with calcium carbonate. It forms long transparent, rectangular columns which soon lose their transparency and become opaque, and lose part of their water of crystallization.

0.7069 gram of this salt lost 12.72 gram water at 100°.

calculated for



Found

6H₂O

17.93

17.99

0.1913 gram anhydrous salt gave 0.0526 gram

CaSO₄

calculated for

Found



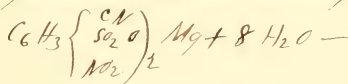
Ca

8.09

8.09

e. The Magnesium Salt

Magnesium Dicyanogenesulphate.



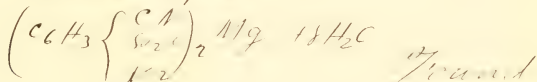
This salt is formed by treating the silver salt with Magnesium chloride. It crystallizes in prisms which are somewhat elongated. It is extremely soluble in

water and contains 8 molecules of
water of crystallization, of which it
loses $3\frac{1}{2}$ on sulphuric acid

0.3500 gram of this salt lost 0.044 gram H_2O at 200°

" " " " " 0.0882 " " at 200°

calculated for



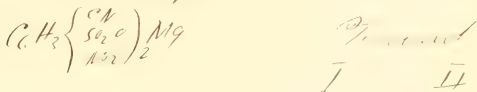
$3\frac{1}{2} H_2O$ - 13.01 13.00

8 " 23.12 23.21

0.1695 gram of the anhydrous ^{salt} gave 0.0411 gram H_2O at 200°

0.2116 " " " " " 0.0493 " "

calculated for



Mg 5.09 5.31 5.09

Magnesium salt of the dinitrobenzoic acid $\left(C_6H_3 \left\{ \begin{smallmatrix} CN \\ SO_2O \end{smallmatrix} \right\} \right)_2 Mg \cdot 6\frac{1}{2} H_2O$

The salt is formed by heating ortho-
nitrobenzoic sulphimide with Magnesium
carbonate. The salt forms beautiful
transparent crystals which seem to
be a combination of orthorhombic
prisms and prisms. These crystals
soon lose their lustre and become
opaque. The salt contains $6\frac{1}{2}$ mol-
ecules of water of crystallization

0.2672 gram of the salt lost 0.1527 gram $\frac{1}{2}$ mol ¹⁸⁰
1.2934 " " " " " 0.2570 " " " "

Calculated for
 $(C_6H_5 \begin{Bmatrix} CO \\ SO_2 \end{Bmatrix} N)_{11} Mg + 6\frac{1}{2} H_2O$ Found
 I II

$6\frac{1}{2} H_2O$ 19.64 19.60 19.87

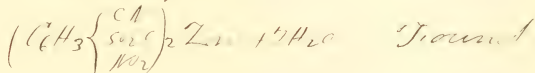
0.2165 gram of the anhydrous salt gave 0.0523 gram ^{MgSO₄}

Calculated for
 $(C_6H_5 \begin{Bmatrix} CO \\ SO_2 \end{Bmatrix} N)_{11} Mg$ Found
 119 5.109

1. Zinc Salt.

Zinc Diamminedinitrogen sulphide
 $(C_6H_3 \begin{smallmatrix} CH \\ SO_2 \\ NO_2 \end{smallmatrix})_2 Zn \cdot 17H_2O$ - 44.00 g. found
 when the silver salt is
 heated in zinc chloride. It forms
 long prismatic columns, is extremely
 soluble in water and contains 17
 molecules of water of crystallization.
 0.7453 gram of this salt lost 0.1477 gram
 H_2O at 170°

calculated for

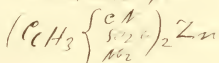


$17H_2O$ 19.52 19.82

0.2064 gram of the (very heavy) salt gave 0.318 gram ZnO

0.1700 " " " " " " 0.0264 "

calculated for



Found

1 14

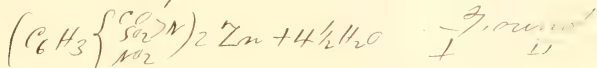
Zn 12.60 12.38 12.48

Zinc salt of the Sulphinate, $C_6H_3\left\{\begin{smallmatrix} CO \\ SO_2 \end{smallmatrix} N\right\}_{NO_2} Zn + 4\frac{1}{2}H_2O$

This salt is formed by treating diamalut benzene sulphonate with zinc carbonate. It forms short thick prisms combined with domes, and resembles very much the corresponding magnesium salt. It contains $4\frac{1}{2}$ molecules of water of crystallization.

0.1861 gram of this salt lost 0.0254 gram H_2O at 125°
 0.4327 " " " " 0.0593 " " " "

calculated for



$4\frac{1}{2} H_2O$ 13.49 13.65 13.71

0.2102 gram of the anhydrous salt lost 0.0328 gram Zn

calculated for



Found

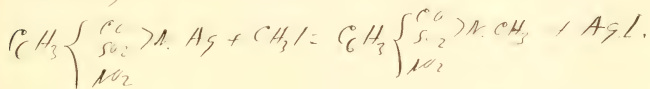
Zn 12.60

12.514

g. Ethereal Salts.

The Methyl Salt of the Sulphinide $(C_6H_3)_{S_2}^{CO} N. CH_3$

This salt is formed by heating the silver salt of paramethanizonic sulphinide in a sealed tube, ^{at 100°} with methyl iodide.

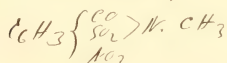


The methyl salt is extracted with boiling alcohol. On cooling the salt crystallizes in leaf-like crystals. It is readily soluble in hot alcohol but difficultly soluble in cold alcohol; it is also soluble in water. It melts at 179° (Uncorr.).

0. 1575 gram of this salt gave 14.73 cc N.

0. 1561 " " " " " 14.25 " "

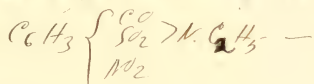
Calculated for



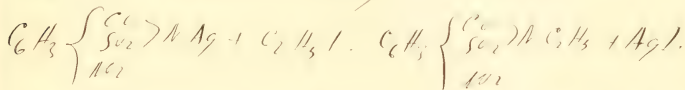
	Calculated for	Found	"
N	11.59	11.77	11.49

From the product of the action of methyl iodide upon the silver salt of paranthiocyanbenzoic sulphonic acid nothing definite has been obtained.

The Ethyl Salt of the Sulphonate



This salt is formed when the silver salt of the sulphonate is heated in a sealed test at 100° with ethyl iodide.



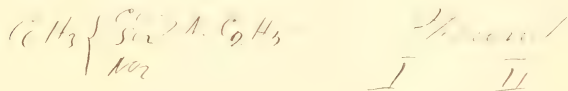
The mass is extracted with boiling alcohol, filtered, and allowed to cool, when a mass of needles resembling dinitrobenzene is obtained. It is readily soluble in hot alcohol but slightly soluble in cold alcohol.

in water, It melts at 172° Uncon

0.1307 gram of the salt gave 13.53 cc N.

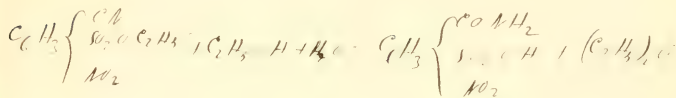
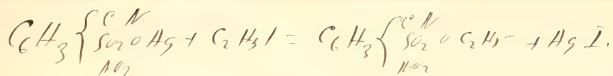
0.1645 " " " " " 14.68 " "

Calculated for



N. 10.97 11.26 11.21

From the silver salt of paracyanobenzene sulphonic acid I have been unable to obtain an ethereal salt by the action of ethyl iodide, but have obtained a substance which is strongly acid, the nature of which has not yet been determined, but is probably analogous to the orthocyanaminesulphonic acid obtained by Fischer¹ by the action of alcohol on orthocyanobenzene sulphonic acid.



VII. Paramecyanbenzenesulphonic Acid.

$\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{CN} \\ \text{SO}_2\text{O} \end{array} \right. \text{H}, \text{H}_2\text{O} -$ This acid is formed when its silver salt is treated with hydrochloric acid enough to precipitate all the silver. It is also formed when the barium salt is precipitated with sulphuric acid. The acid crystallizes in long prisms which contain one molecule of water of crystallization. If heated very rapidly, it melts between 143° and 150° but solidifies again immediately. This is due to the fact

fact that the acid goes in solution in its water of crystallization and when this is driven off it solidifies. It is extremely soluble in water, being soluble in less than its own weight. On being neutralized with potassium carbonate the potassium salt of *para*-tricyanbenzenesulphonic is obtained. On boiling the acid with hydrochloric acid the acid ammonium salt of *para*-tricyanbenzenesulphonic acid is probably obtained for when an excess of caustic potash is added ammonia is liberated, and then on adding an excess of hydrochloric acid a mass of fine needles is obtained resembling the acid potassium salt of *para*-tricyanbenzenesulphonic acid.

When the acid is heated at 130° it loses one molecule of water and if the temperature is then raised to 150° it begins to increase in weight. This increase is probably due to the oxidation of the cyanogen group.

This product is still under investigation.

6. 3603 gram of the acid lost .0254 gram H₂O at 130°

0 2503 " " " " Jave. 02861 Grams A.

0.3033 " " " " " 0.3403 " "

Calculated for

$$CH_3 \begin{cases} CN \\ SO_2OH + H_2O \\ NO_2 \end{cases} \quad \text{found}$$

H₂O 7.31

7.06

11.42

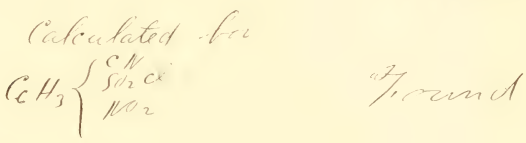
11.43 11.23

III Paramitocyanophosphorochloride $C_6H_3 \left\{ \begin{smallmatrix} CN \\ SO_2Cl \\ NO_2 \end{smallmatrix} \right.$ -

This chloride is formed when the potassium salt of the paramitocyan benzenesulphonic acid is treated with phosphorus pentachloride. One molecule of the potassium salt is mixed with one molecule of phosphorus pentachloride and the mixture heated to a temperature of 140° in a sulphuric-acid bath for several hours. The mass is then treated with water to decompose the phosphorus pentachloride and to dissolve the potassium chloride. The chloride is then dissolved in chloroform and dried by means of calcium chloride. The chloroform solution is allowed to evaporate and the

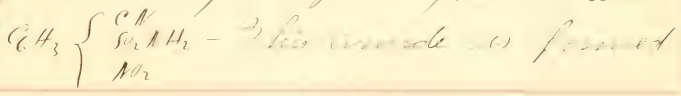
chloride crystallizes in long rectangular prisms which melt at 107°-108° Uncon. They are soluble in chloroform, ether and benzene.

0.2640 gram of this chloride gave	0.2538 gram Base
0.1640 " " " " " "	0.1372 " "
0.2025 " " " " " "	18.73 cc N.
0.1640 " " " " " "	0.0914 grams Agcl
0.2640 " " " " " "	0.1344 " "
0.1003 " " " " " "	0.0392 " "



Cl	14.38	14.83	14.46	14.59
N	11.40	11.63		
S	13.00	13.23	13.19.	

IX Paranitro cyanobenzene sulphamide

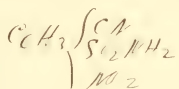


When para-nitro cyanbenzenesulphor chloride is treated with ammonia, 2 grams of the chloride were dissolved in chloroform and an aqueous solution of ammonia added. The mixture is shaken in a separating funnel occasionally. The amide separates as an amorphous mass, which is filtered off and recrystallized from alcohol. It crystallized in small rectangular blocks resembling cane sugar. It does not melt below 270° yield excellent.

0.1920 gram of this salt gave 28.02 c.c.N.

0.1535 " " " " " 22.79 " "

Calculated for



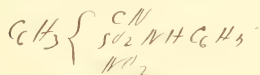
Found

N.	18.33	18.54	18.65
----	-------	-------	-------

X *Phenylglyoxal dihydrazide* $C_6H_5 \left\{ \begin{smallmatrix} CN \\ NH_2 \end{smallmatrix} \right\}_2$

This anilide is formed in the same way as the amide. Dissolve 1 gram of the chloride in chloroform and add aniline, then cover the mass with water and heat the mixture to drive off the chloroform. As the chloroform is evaporated the anilide separates as a powder. This powder is recrystallized from alcohol. The yield in this case is in that of the amide is theoretical. The anilide crystallizes in fine needles and melts at $207-208^\circ$ (Uncon).

0.1513 grams of this anilide gave 16.97 cc N
calculated for



found

N. 13.94

14.17

XI Action of Aniline on the Chloride of Pararibonitrosulfonic Acid
Action of Aniline on the Monosymmetrical Chloride in the Presence of Water. The unsymmetrical chloride was added to an excess of aniline in an emulsion in water; 4 gram of chloride in 30 cc of water. The mixture was shaken until no more aniline was taken up. The excess of aniline was then distilled off in a current of steam. The liquid was removed by filtration and from the filtrate aniline hydrochloride and the aniline salt of pararibonitrosulfonic acid were obtained. The residue insoluble in water was dried and extracted with chloroform. The chloroform on evaporation gave

nearly pure fusible anhydride of
 paranthroorthosulphobenzoic acid.
 The residue from the chloroform extract
 was dissolved in ~~chloroform~~ alcohol
 and was the infusible anhydride. The
 yield of the infusible was only about 3%,
 the fusible anhydride about 20% and
 the amine salt about 20%.

B. - Action of aniline on the chrysogen-
 metrical chloride - $\frac{1}{2}$ gram of
 the ^{new} chrysometrical chloride was grad-
 ually mixed with an excess of an-
 iline. The mixture after being thor-
 oughly ground was heated in the
 water bath for 3 hours, and then
 treated as above. There were obtained
 .4 gram of the fusible anhydride and less
 than .1 gram of the infusible.

C. Action of Aniline upon the chrysogen-

nitric chloride in chloroform solution.
 .5 gram of the ~~unsymmetrical~~ chloride
 was dissolved in chloroform and an
 excess of aniline added to the solution.
 The solution was heated to drive off
 the chloroform, and then heated at 100°
 for an hour. The mass was then heated
 as a.p.s. From the water solution .4 gram
 aniline salt of parametacorthosulfon-
 itic benzoic acid, and .23 gram of
 the fusible anilide. In another
 experiment in which I used the last
 of the chloride, the chloride was
 dissolved in chloroform and ^{aniline} ~~aniline~~
 added in excess. The mixture was ^{kept cold and} shaken
 for a short time. The precipitate which
 formed was fitous and washed with
 chloroform; the precipitate was pure
 infusible anilide. The filtrate was

heated and from it consisted of the infusible anilide and aniline hydrochloride. The chloroform solution was then heated and from it the fusible anilide and a small quantity of the infusible anilide were obtained.

Action of Chloroform on the Symmetrical Chloride - ^{in presence of water} When the symmetrical anilide is treated with an excess of aniline in water, chloroform or ether the only products obtained are the fusible anilide and aniline hydrochloride. If the chloride is mixed with aniline and heated in the proportion of one molecule of chloride to one of aniline, the anil is formed; if in the proportion of one molecule of the chloride to two molecules of aniline the anil is formed together with a

a very small amount of the fusible anhydride; when the proportion is one molecule of the chloride to four molecules of aniline only the fusible anhydride is obtained.

XXI. Fusible Anhydride - This is formed best by treating the unsymmetrical chloride dissolved in chloroform with an excess of aniline. The solution must be kept cold as the yield of this anhydride is diminished by warming the solution. The infusible anhydride is precipitated together with aniline hydrochloride in the chloroform solution. This precipitate is dried, and washed with water to dissolve the aniline hydrochloride, and the residue is found to be pure infusible anhydride. It is insoluble in water. Soluble in alcohol. (Some recent work)

seems to show that this amide undergoes a change by boiling it in an alcoholic solution. This is still under investigation. The product analysed was the white precipitate insoluble in water. It does not melt on heating to 250° . It is soluble in caustic potash but differs from the infusible amide of α -thio sulph. benzoic acid in that it is decomposed by it. This substance on analysis gave the following results.

0.1735 gram infusible amide gave 0.018263 gram
 0.1818 " " " " 0.019221 " "
 0.1925 " " " " 0.1156 " BaSO_4
 0.1561 " " " " 0.0907 " "

calculated for
 $\text{C}_6\text{H}_5\left\{\begin{array}{l} \text{C}(\text{NH}_2\text{C}_6\text{H}_5)_2 \\ \text{SO}_2 \end{array}\right\} 70$

found

N	10.58	10.53	10.58
S	8.06	8.25	7.98

It was impossible to get it to crystallize except as stout like masses.



211 Fusible Anilide This is found
in all cases (in part) in which an
excess of aniline is used. It is
the only product formed when
an excess of aniline acts on the
symmetrical chloride. In one ex-
periment in which some infusible an-
ilide was boiled in alcohol it was
found to have been changed into the
fusible anilide. This is still under in-
vestigation. The anilide crystallizes
from chloroform in a silky mass.
It is soluble in alcohol, insoluble in
water. It is dissolved by alkalis and
reprecipitated by acids; by this means
it can be obtained free from the anil
and the infusible anilide. It melts
at 222° (Hacm).

This salt on analysis gave the following results



0.2455 gram fusible aniline gave 0.5158 gram CO_2
 0.2455 " " " " 0.0871 " H_2O
 0.1502 " " " " 0.0897 " BaSO_4
 0.2016 " " " " 17.4°C N.
 0.7035 " " " " 17.50 " N.

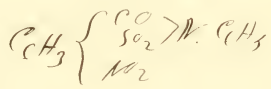
Calculated for					
C_6H_3	CONHCH_3	I	II	III	IV
	SO_2NHCH_3				
C	57.40	37.34	—	—	—
H	3.78	3.93	—	—	—
S	8.06	—	8.21	—	—
N	10.61	—	—	10.54	10.80

XIII The Anil - This is formed when
 aniline and the symmetrical
 chloride are heated together in the
 proportion of one molecule to of
 the chloride to one molecule of aniline.
 Add the chloride gradually to the aniline and
 heat the mixture some time in a

Sulphuric acid bath. The mass is then extracted with boiling alcohol. From the alcoholic solution the acid is obtained; it crystallizes in fine needles: it is insoluble in alkalis and by this means it can be separated from the anhydrides. It melts at 183° (Mura). On analysis it gave the following results

0.1562 gram of the acid gave 0.1199 gram BaSO_4
 0.1735 " " " " " 0.1314 " "
 0.2105 " " " " " 15.82 cc N.
 0.2124 " " " " " 15.67 " "

Calculated for



Found

S	10.52	10.55	-10.41
N	9.21	9.44	9.27

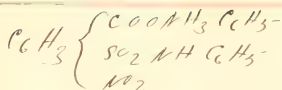
X)

~~XX~~ Acidic salt of Para nitro the sulphuric acid.

benzoic Acid This is the fourth
aniline derivative formed by the ac-
tion of aniline upon the chloride
of para nitro the sulphuric acid.
Its formation is doubtless due to
some secondary reactions. It is
readily soluble in water; from which
it crystallizes in fine flakes; on analysis
it gave the following results

0.2664 gram	gave	0.5393 gram CO_2	+ 0.1029 gram H_2O
0.2156 "	"	0.4411 "	" + 0.0836 "
0.1428 "	"	0.2787 "	BaSO ₄
0.1434		0.0793 "	"
0.2000 "		16.56 cc N	
0.2004 "		16.80 cc N	

calculated for



2. *Paratoluidine*

C	54.91	55.23	55.03	—	—	—	—
H	4.10	4.29	4.35	—	—	—	—
N	10.15	—	—	10.40	10.55	—	—
S	7.71	—	—	—	—	7.60	7.58

Reaction of Paratoluidine & the chlorides—The symmetrical and unsymmetrical chlorides were heated ~~with~~ in exactly the same way with paratoluidine. On using an excess of paratoluidine the same product was obtained from both chlorides.

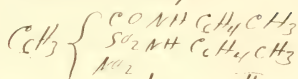
Paranitrochrosulphonic toluidide (Hua)

This is prepared by treating either the symmetrical or the unsym-

metrical chloride with succin-
 telenidin in chloroform solution
 or grinding them up together.
 It crystallizes from alcohol in
 fine slightly yellow needles which
 melt at 234° (Uncor.). It is read-
 ily soluble in hot alcohol diffi-
 cultly soluble in cold alcohol. It
 is dissolved by alkalis and repre-
 cipitated by acids. It was found
 impossible to make any compound
 analogous to the infusible amide.
 On analysis it gave the following
 results

0.2497 gram	gave	0.5433 gram CO_2	and	0.1019 gram H_2O
0.2576 "	"	0.5617 "	"	0.1077 "
0.2022 "	"	16.46 $^{\circ}\text{C}$	N.	
0.2078 "	"	16.97 "	"	
0.1610 "	"	0.0863 g	Basor	
0.1805 "	"	0.1008 "	"	

Calculated for



		I	II	III	IV
C	59.27	59.34	59.47		
H	4.48	4.54	4.47		
N	9.91			10.22; 10.26	
S	7.53				7.37 7.67

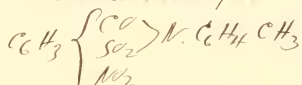
Mononitrobenzyl chloride, Nitro (para) -

b. Para Nitro. This is formed by treating the symmetrical Chloride with para toluidine in the proportion of one molecule of the Chloride to one molecule of the toluidine. The mixture is heated in a sulphuric acid bath for about an hour. The mass is then extracted with boiling alcohol. On cooling the Nitro crystallizes from the alcohol in fine needles which melt at 164° to 165° (Uncorr.). It is soluble in hot alcohol; insoluble in water and alkalis.

On analysis it gave the following results.

0.1042 gram substance	gave	0.0761 gram BaSO_4
0.1061 " "	" "	0.0786 " "
0.1062 " "	" "	7.55 c.c. N_2
0.1065 " "	" "	7.62 " "

Calculated for



Found

S	10.06	10.04	10.19
N	8.83	8.93	8.99

XIII Conclusion

Several conclusions seem to be justified by the results of the experiments described in this paper.

1. When phosphorus pentachloride

acts upon para nitrobenzo sulpho
benzoic acid two isomeric chlorides
are formed, one of which has
the formula $C_6H_3 \begin{cases} C(Cl)_2 \\ SO_2^O \end{cases}$ and melts
at $56-57^\circ$ (Uncor) the other has
the formula $C_6H_3 \begin{cases} COCl \\ SO_2^O \end{cases}$ and melts
at $74-75^\circ$ (Uncor).

II When the two chlorides are treated
with ammonia, the first, a un-
symmetrical gives the ammonium
salt of para nitro cyanobenzene sul-
phonic acid; the other gives the
ammonium salt of para nitro
benzoic sulphimide.

III When the silver salts are treated
with hydrochloric acid the silver
salt of para nitro cyanobenzene sulpha-
ic acid gives the free cyan para nitro
cyan benzene sulphonic acid, while

the silver salt of the sulphinate
gives paramethoxybenzenesulphinate

III When the silver salts are treated
with methyl and ethyl iodide, the
silver salts of the sulphinate yield
ethereal salts while the silver salt
of the paramethoxybenzenesulphonic
acid yields a product which is
strongly acid. The nature of this
product has not yet been deter-
mined.

V. When the two chlorides are treated
with acetic anhydride the symmetrical chlo-
ride yields an acid and a fusible
anhydride while the unsymmetrical
yields an infusible anhydride which seems
to be easily decomposed. It also
yields the fusible anhydride.

VI With parabromochlorine both chlorides

Yield the same toluide.

XI^{III} Biographical.

George William Gray, the author of this Association, was born at Cumberland Mch. on August 12, 1867. He was educated in the public schools of Maryland and Washington, D. C. He entered Johns Hopkins University in 1887 and graduated from there in 1890 having pursued the chemical-physical course. From 1891-1892 he was with the Baltimore Sugar Refining and the Maryland Steel Company as chemist. He returned to Johns Hopkins University in the fall of 1892 and since that time has pursued advanced courses in chemistry.





